PHYSICO-CHEMICAL BEHAVIOUR OF AQUEOUS AND NONAQUEOUS SOLUTION OF AMPHIPHILIC MOLECULES IN PRESENCE OF ADDITIVES

DISSERTATION

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The dissertation entitled "Physico-Chemical Behaviour of Aqueous and Non-Aqueous Solutions of Amphiphilic Molecules in Presence of Additives" by Miss Kirti, is suitable for submission for the degree of Master of Philosophy in Chemistry.

(KABIR-UD-DIN)

Dedicated
To the Memory of
(Late) PROF. H. N. SINGH

C O N T E N T S

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KIRTI

INTRODUCTION

The domain of surface science is perhaps one of the most interdisciplinary areas of modern science and technology[1]. Although the importance of surface science has been recognized for more than a century, it is only during the last few decades that rapid advances in the understanding of surface phenomena have taken place. When one looks closer to the earth, one finds that it is full of objects, and that each object is surrounded by a surface or an interface. Fortunately, all the interfaces can be grouped in five major classes, namely, gas/liquid, liquid/liquid, solid/liquid, solid/gas and solid/solid (Fig. 1). All objects are surrounded by one or more of these basic five interfaces. All of these interfaces have a common property called surface tension or surface free energy. There is a class of compounds called surface active compounds[2,3] (or surfactants) that decreases strikingly the surface tension or surface free energy of these interfaces.

Surfactants, surface active agents, or detergents are amphiphilic, organic or organometallic compounds having two distinct parts, namely, a hydrophilic (water soluble) or polar part, and a lipophilic(oil soluble) or non-polar part[4-7]. The lipophilic part is generally a long hydrocarbon chain. Depending on the chemical structure of the hydrophilic moiety bound to the hydrophobic portion, the surfactant may be classed as cationic, anionic, nonionic, or ampholytic (zwitterionic)[8-12]. An exhaustive list of both synthetic

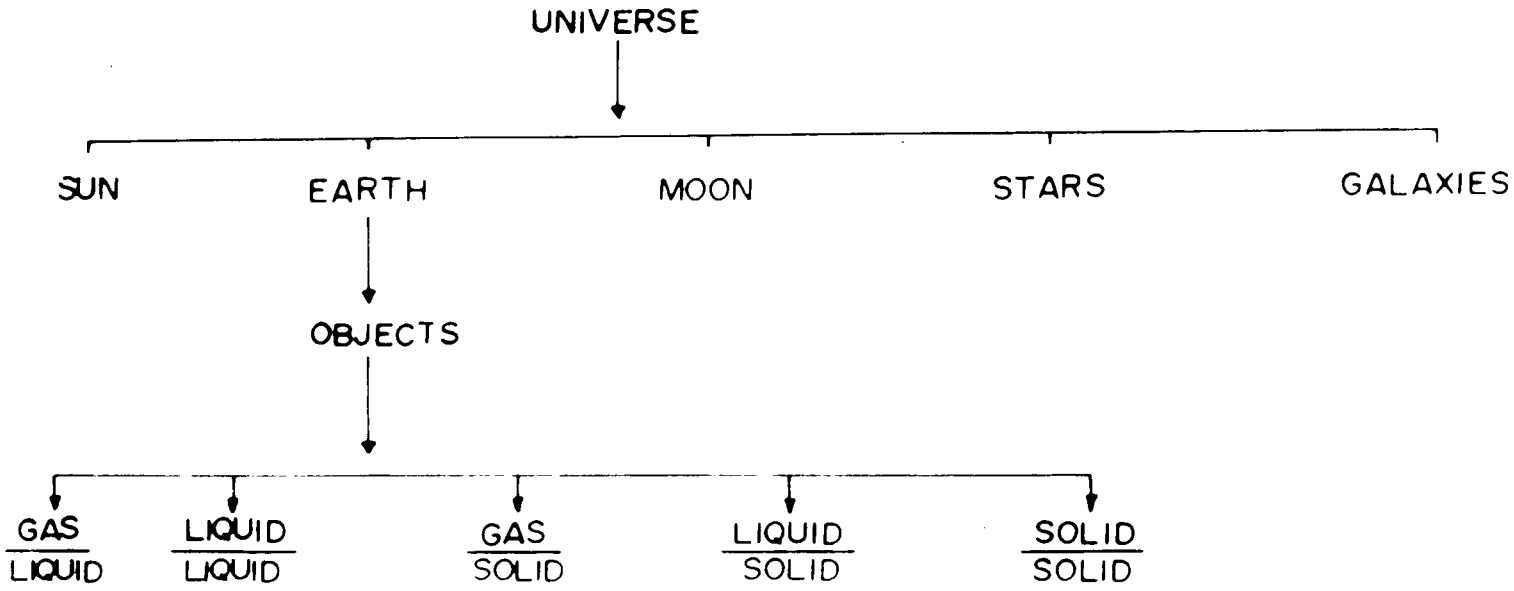


Fig. No. 1 : The five interfaces.

and naturally occurring surfactants is available. Their preparation and properties in general have been given in the excellant monograph of Feiddler and Fendler[13]. The characteristic properties of surfactants in solution which render possible their practical applications such as washing, cleaning, wetting, emulsifying, dispersing and foaming depend in all cases on the tendency of these compounds to accumulate at interfaces between the solution and the adjacent gaseous, liquid, or solid phases[14].

Surfactant molecules form association colloids or micelles in solution with in a fairly narrow concentration range. Micelle do not exist at all concentrations and temperatures. There is a very small concentration range below which aggregation to micelle is absent and above which association leads to micelle formation. This concentration is called critical micelle concentration (CMC). The number of molecules that aggregates to form micelles is called the aggregation number. Micellar aggregation can be demonstrated by measurements of physical properties against surfactant concentration. The most significant property is surface (or interfacial) tension (Fig. 2).

The reason 'why do micelles form' may be explained by taking into account the changes occuring when a monomer is transferred from its aqueous environment in to the micelle. On transferring the monomer in to micelle, the

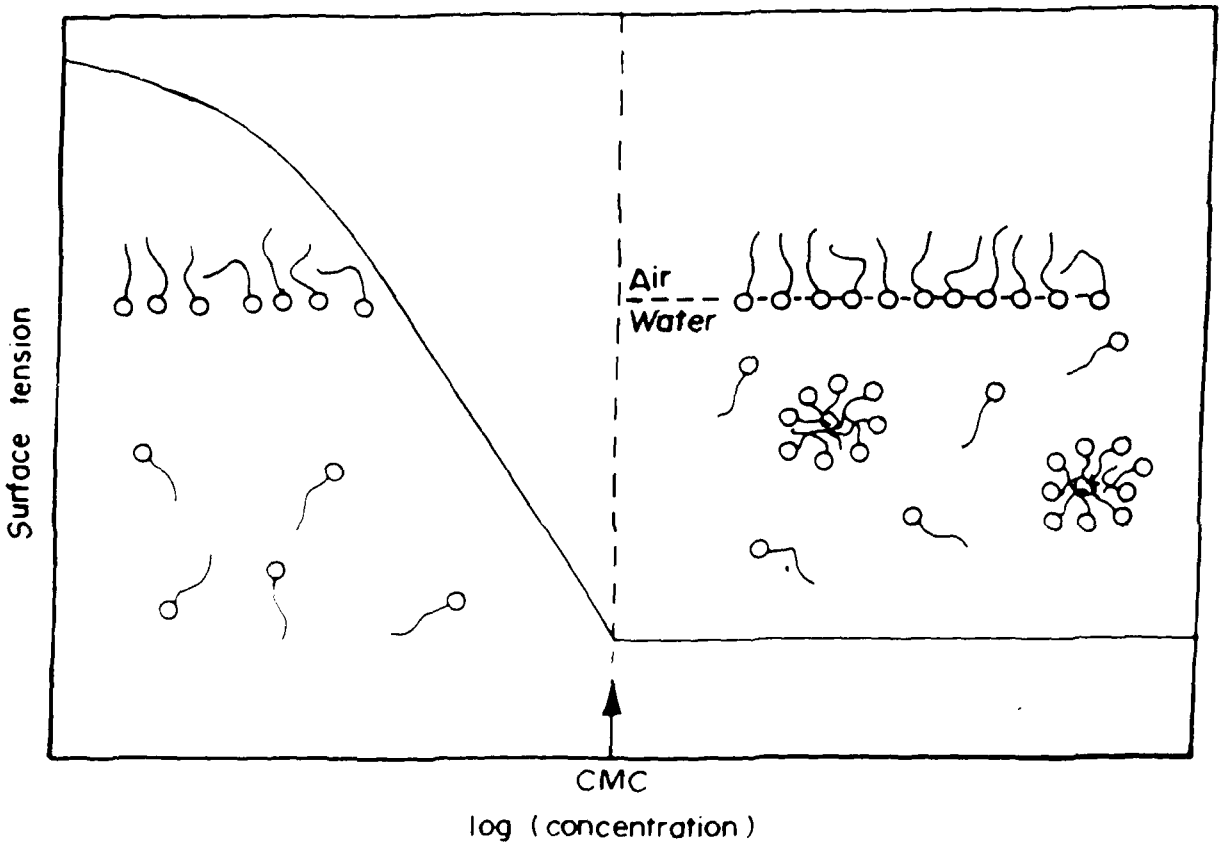


Fig. No. 2 : Surface (air-water) tension as a function of surfactant concentration for an aqueous micellar solution. Schematic structure of the solution is shown below and above the critical micellar concentration (CMC)

high energy of the hydrocarbon/water interface is lost, as the chain is now in contact with others of a like nature. Transfer of monomer in to micelle also means that the structuring of water around the hydrocarbon part of the monomer is lost, therefore an ordered state has become a disordered one with regard to the water, implying a positive entropy change and a decrease in free energy. The factor opposing the micelle formation in ionized surfactants is rise in free energy due to electrical work and translational freedom losses due to incorporation of monomer in to a micelle. This disorder to order transition gives a negative entropy change which will oppose the positive entropy changes occuring from loss of water structure. The overall decrease in free energy due to loss of hydrocarbon/water interfacial energy and water structure outweighs the free energy rise due to electrical work and translational freedom losses, giving a remarkable tendency to micellise. Mukerjee and Mysels[15] have compiled CMC data of various class of surfactants using different techniques.

Normal Micelles

Aggregate formed in aqueous solutions of surfactant molecules at CMC are known as normal micelles. They are always in dynamic equilibrium. Such micelles are thought to be roughly spherical[16-18]. A schematic two dimensional representation of an ionic spherical micelle is shown

in Fig. 3. In the case of ionic surfactants, part of the counterions are "bound" to the surface of the micelle, forming what is called the "Stern layer", whereas the remaining counterions are localized at greater distances from the surface of the micelle, in what is called the "Gouy-Chapmann electric double layer".

Results of light scattering, viscosity, diffusion and ultracentrifugation studies on nonionic cetomacrogol micelles indicated their shape to be ellipsoidal with an axial ratio of 2:1[20]. Some water molecules may be entraped by the micelle[21,22] and under certain circumtances part of the hydrocarbon chain may extend into the aqueous phase[23]. The amount of water in the micellar interior varies from surfactant to surfactant, but water is considered, at present, to penetrate the micellar surface only up to distances of approximately three to six carbon atoms[21,23-25]. The interior, or core, of the micelle has generally been inferred to be hydrocarbon-like from esr[26] and nmr[21,27] spectroscopy and from the utilization of fluorescent probes[28].

Reverse Micelles

Surfactants in non-polar solvents, in the presence of traces of water, associate to form the so called "reverse" or "inverted" micelles. The structure of the micelle is reversed, the polar head groups of the monomer

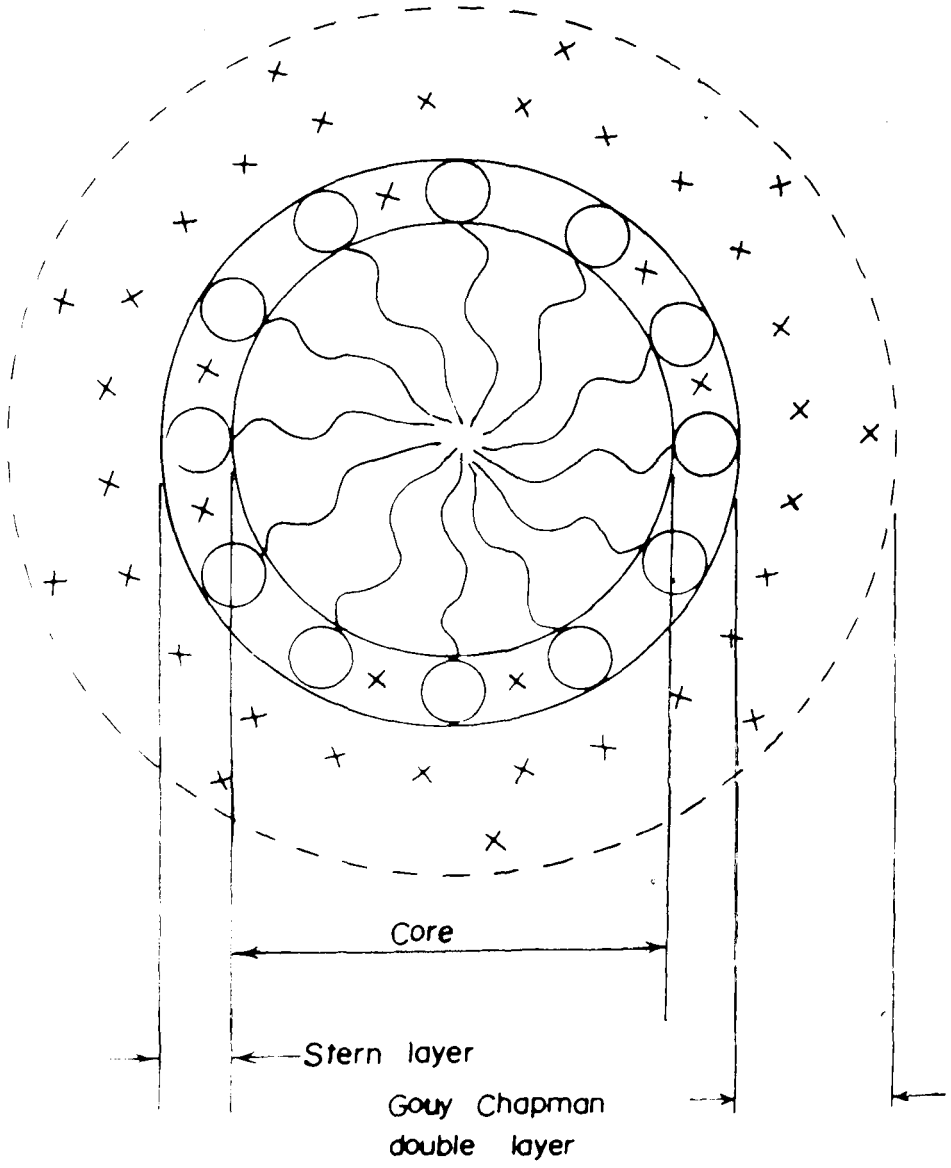


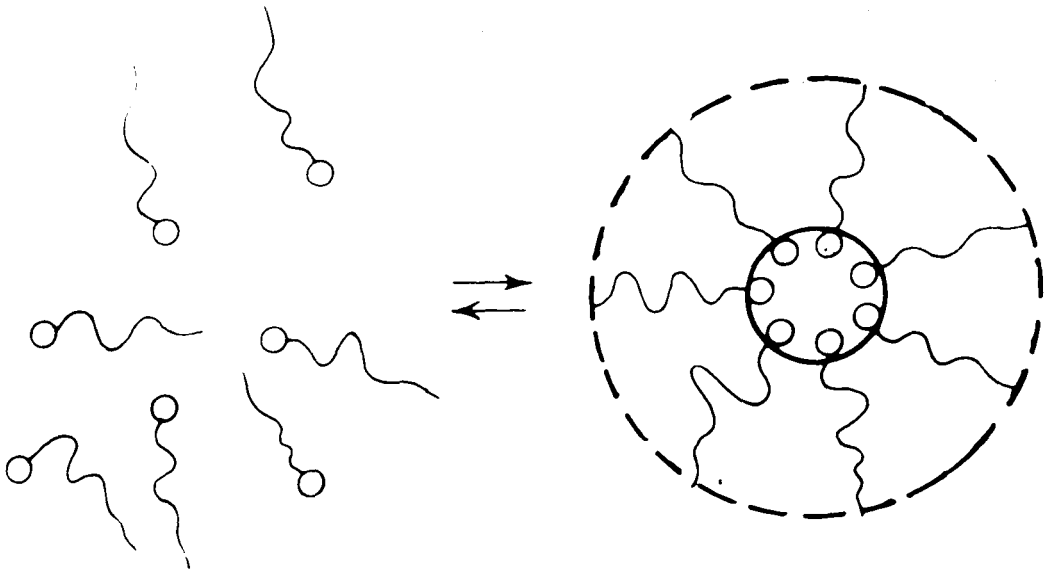
Fig. No. 3 : A two-dimensional schematic representation of the regions of a spherical ionic micelle. The counterions (X), the head groups(◯), and the hydrocarbon chains (∼∼) are indicated.

being present in the centre of the micelle, and the hydrocarbon chains extending outwards into the solvent. Such micelles could be formed in presence of traces of water which forms a water pool in the interior of the micellar aggregate. The size and properties of reverse micelles vary with the amount of water present[29-32]. A possible structure of reverse micelle in a nonpolar medium in equilibrium with monomer is shown in Fig. 4.

The discontinuity in some physical property (viscosity, solubility, surface tension,etc.) of the solution can be used to identify the CMC, and techniques such as scattering, ultracentrifugation and viscosity are used to determine the size and shape of the micelle. Some other techniques which have been developed to determine the CMC include dye solubilization[33,34], water solubilization[35], nmr[36,37]. The different experimental methods available for determining the CMC are given in the compilations of Shinoda et al.[17], Elworthy et al.[18]and Mukerjee and Mysels[15].

Mixed Micelles

The formation of micelles from more than one chemical species gives rise to what are known as mixed micelles. In the simplest case, binary or ternary mixtures of surfactants of similar, but not identical chain lengths may be studied and the thermodynamics of this type of



Monomer solution
(Ideal solution)

Micelle
(Hydrocarbon part)
(Nonideal solution)

FIG. No. 4 : REVERSE MICELLE

micelle formation has been described[38,39]. Clint[40] developed an analytical description which included both micelle composition and monomer concentration above the mixed CMC for mixtures of nonionic surfactants. Clint's treatment assumed ideal mixing in the micelle. Furthermore, the expression of Lange and Clint[40,41] for the CMC values of mixtures of nonionic surfactants has been experimently verified for cases where ideal mixing might be expected[40,4] The properties of the mixtures of an anionic surfactant and a nonionic surfactant[42,43], and cationic and nonionic surfactants[44] have been interpreted with the aid of mixed micelle formation between the surfactants. Lange and Beck[41] and Clint[40] pointed out that the CMC of the mixed micelles is lowered more than that of the single surfactant.

Another class of mixed micelles results when low molecular weight molecules are solubilized by micelles formed from surfactants containing a relatively larger non-polar chain. The solubilized substances, also called a penetrating additive[45], may be located in the hydrocarbon core[46] or the hydrophilic mantle[47-49].

Structural aspects of surfactant micellar systems : Influence of additives

Surfactant molecules can be considered as building blocks. Surfactant self-association in aqueous media is strongly cooperative and starts generally with the

formation of roughly spherical micelles around the critical micelle concentration. When the surfactant concentration markedly exceeds the CMC, the shape of the spherical or ellipsoidal micelle undergoes gradual changes[50,51]. Figure 5 schematically shows various structures that are formed upon increasing the concentration of surfactant. In the beginning of structural changes spherical micelles become cylindrical. Upon further increasing the concentration, there is a hexagonal packing of water cylinders. Upon addition of an oil and a short-chain alcohol, one can convert such water cylinders into water-in-oil (w/o) microemulsions.

It is possible to induce a transition from one structure to another by changing the physico-chemical conditions such as temperature, pH, addition of ionic and nonionic solutes, in the surfactant solution[18,52-58]. The rod shape structure fits the results for dimethyldodecyl amineoxide micelles in salt solutions at low pH values[54]. For ionic surfactant systems, micellar growth increases very strongly with decreasing temperature, with increasing counterion size (Cl^-, Br^-, I^-) and with the addition of salts[55-57]. For nonionic micelles, raising the temperature favours micellar growth[58].

Since micelles are dynamic structures comprising a liquid core, it is probably unrealistic to regard them as rigid structures with a precise shape[59]. The shape

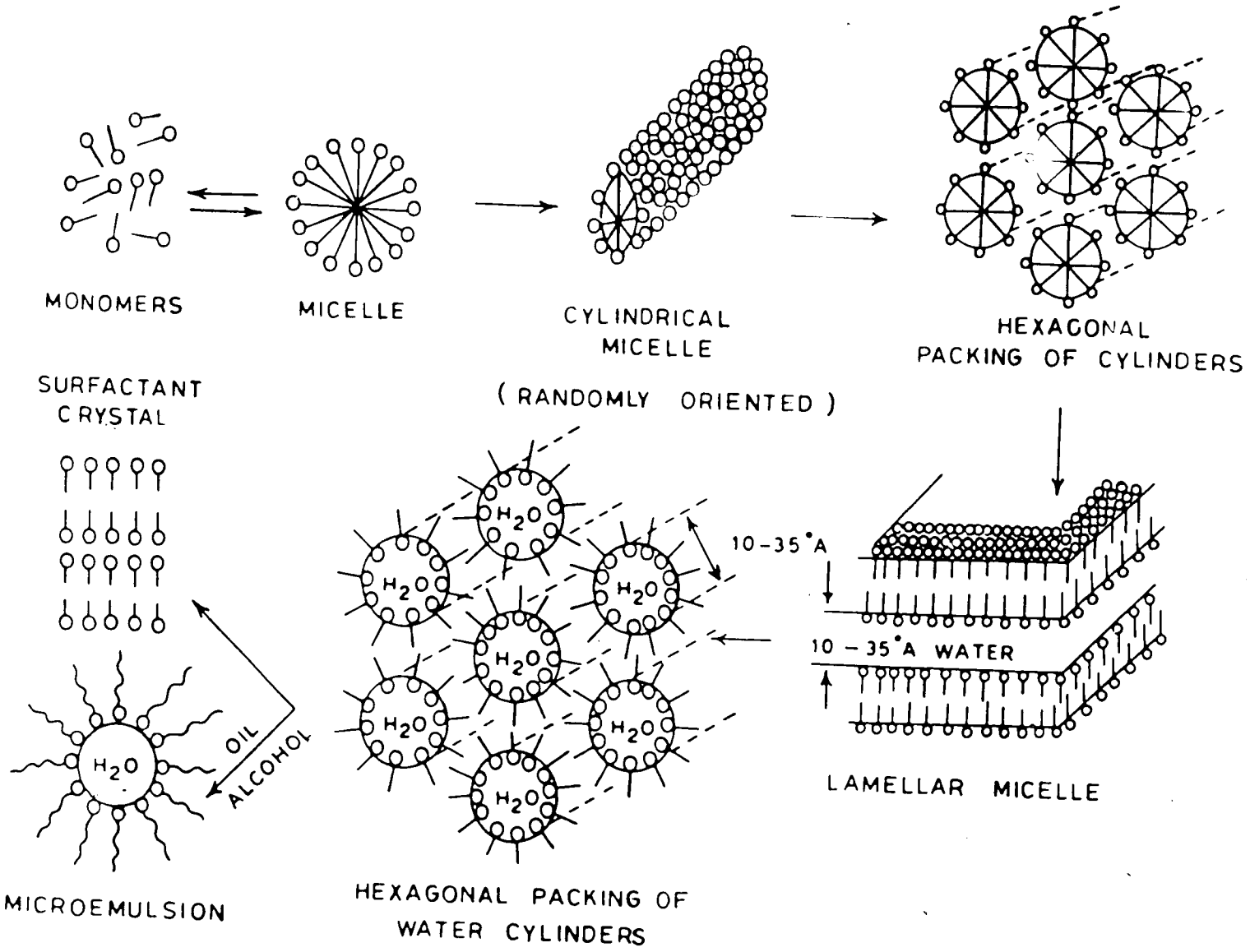


Fig. **No. 5** : A schematic illustration for the formation of various structures in surfactant solution upon increasing the concentration of surfactant

and size of these micellar aggregates can, in principle, be determined by various methods, such as light scattering[60-62], diffusion, sedimentation velocity, sedimentation equilibrium[63,64], ultrasonic absorption[65], time resolved fluorescence[66,67], etc. Viscometric technique has been used in a number of experimental investigations[51,56,57,68-70] of micellar solutions both because of its simplicity and its sensitivity to detect changes in the size of the anisotropic micellar aggregates. The sphere-to-rod transitions of ionic and nonionic micelles have been studied by a number of workers[60,51,55-57,61-71]. For sodium dodecyl sulphate and for a series of cationic surfactants in NaCl solutions, a sharp break in apparent micelle molecular weight is observed when the NaCl concentration reaches a value of 0.45 M and the break point would correspond to the sphere-to-rod transition[72,73]. The micellar sphere-to-rod transition is highly dependent upon the nature of the counter ions and was concluded that strong counterion binding promotes the transition from small spherical to cylindrical micelles[56,74].

Temperature affects the sphere-to-rod transition. The viscosity of the cylindrical micellar solution decreases with the increase in temperature due to the breaking up of the cylinders to smaller aggregates[57]. Decrease in micellar size with temperature at high concentrations of electrolytes has been reported by various authors[57,75,76].

Importance of Micellar Solutions

Micellar solutions are known to increase the solubility of slightly soluble or insoluble organic compounds in water[13,18]. Micellar solutions are used extensively in synthetic, analytical, pharmaceutical and industrial chemistry. The change in the micellar structure have pronounced effects on micellar catalysis[77]. Several reports on the structures of micelles of cetyltrimethylammonium bromide (CTAB) have recently appeared[45,49], and this micelle has been used to catalyse a variety of reactions[77-79].

The engineering applications of surface science range from agricultural sprays to oil recovery including areas such as catalysis, coating, dispersions, electronics, floatation of minerals, lubrication, and retardation of evaporation from lakes and reservoirs.

Among biomedical areas, the applications of surface science extend from anesthesiology to zoology including fields such as artificial implants, biomembranes, biolubrication, lipoproteins, lung surfactant, opthalmology, pharmaceutical and pharmacology. The surface active agents may influence the biological efficacy of the drug or pesticide. Many poorly soluble drugs and pesticides are administered in a solubilized form using micellar solutions in order to increase the bioavailability and targetting to the site of action. Certain surfactants have the ability

to increase the permeability of some bacterial cell walls, and hence are synergistic with some antibacterial agents.

Micellar solutions in reverse micelles play a vital role in removing polar dirt from clothes, in motor oils to solubilize corrosive oxidation products and to prevent them from reacting with engine parts. Solubilized systems are used in removing odour causing molecules from food packaging plants, photographic processes and in surfactant type corrosion inhibitors. A very important application of micellar solution is in separation science[80]. Aqueous micellar systems have the ability to solubilize, compartmentalize and concentrate (or separate) solutes, alter the local environment about associated solutes, alter the position of equilibrium systems and alter the photophysical and chemical pathways and rates among others. Although all of these micellar features can be exploited to aid the separation scientist in specific instances, the main basis for the successful utilization of aqueous micellar media in separation stems from the fact that they can differentially solubilize and incorporate a variety of solutes. Some of these are micellar facilitated sampling considerations, extractions based on the differential solubilizing ability of micelles, micellar electrokinetic capillary chromatography, micellar liquid chromatography, micellar enhanced detection,

micellar enhance ultrafiltration, and micelle mediated extractions or preconcentrations of polyaromatic hydrocarbon.

It is clear from the above mentioned literature that micellar media have attracted wider attention than any other media in recent years. With specific and judicious choice of media, chemical transformations can be carried out more swiftly, under milder conditions with higher yields and fewer by-products and, if necessary, with good stereo and regio-chemical control.

Importance of Research Problem

Increasing attention is being devoted to the study of the "incorporation" or solubilization of neutral organic molecules into micelles in aqueous solutions. Some of the most studied solubilizates are alcohols, because of the important role they have in preparation of microemulsion[81]. It is generally accepted that the medium chain length alcohols intercalate between the surfactant ionic head groups to decrease the micellar surface charge density[82]. This effect is correlated with modification of the growth and shape of the micelles[83]. Recently some linear medium chain aliphatic amines have been getting more recognisation as cosurfactants in microemulsion preparations[84-86]. Despite the significance of amines in microemulsions proper attention has not been paid so far to the contribution of

medium chain normal amines in micellar systems.

Visualizing the significance of micellar structure transitions and their dependence upon the nature of electrolytes[87,88], temperature and, in some cases, the influence of organic additives[89], it was thought worthwhile to persue a study of the effect of aliphatic amines on concentrated micellar solutions in aqueous potassium bromide (KBr). Compared with other techniques, the capillary viscometry method is simple and reliable and can provide a large body of important information with respect to the investigation of the increase in micelle size[90]. The results of studies on the effect of the addition of various aliphatic amines on the viscosity of 0.1 m CTAB + 0.1 m KBr solutions are presented herein. From the temperature dependence of the viscosity, the activation free energies (ΔG^*), enthalpies (ΔH^*) and entropies (ΔS^*) for the viscous flow have also been calculated.

EXPERIMENTAL

(a) Materials :

Cetyltrimethylammonium bromide (CTAB) from E. Merck (98.5%) was recrystallized twice from acetone.

$$CH_3(CH_2)_{15}\ N^+(CH_3)_3Br^-$$

The surfactant was dried after filtration in a hot air oven at 50°C. The purity of the surfactant was ascertained from the absence of minimum in the surface tension versus logarithm of concentration plots. KBr from E. Merck was heated for one hour ($\sim 60^\circ C$) and was kept in a desiccator (P_2O_5) till use.

The amines, viz. n-hexylamine (C_6NH_2), n-heptylamine (C_7NH_2) and n-octylamine (C_8NH_2) (all "Purum grade") were obtained from Fluka, whilst n-butylamine (C_4NH_2) was a Riedel-de-Haen product. All chemicals were used as supplied. Demineralized water, redistilled from alkaline potassium permanganate, was used. The specific conductivity of water was in the range $1x10^{-6}$ to $2x10^{-6}$ $ohm^{-1}cm^{-1}$. Water, equilibrated with atmospheric carbondioxide, was used throughout the work.

(b) Preparation of solutions :

0.1 m CTAB in 0.1 m KBr solution was prepared by dissolving required amounts of CTAB and KBr in a single volumetric flask in distilled water. The concentration of mixed solvent was fixed throughout the work. Different

solutions of amines were prepared in the mixed solvent (0.1 m CTAB + 0.1 m KBr) and the concentrations of amines were calculated as mol per kg mixed solvent.

(c) Viscosity measurements :

Viscosities of the solutions were measured in an Ubbelohde viscometer immersed in a thermostated bath. The relative viscosity of a solution was calculated using the relation :

$$\frac{\eta}{\eta_o} = \frac{t}{t_o} \qquad \ldots\ldots (1)$$

where η and η_o are the viscosities of the solution and water, respectively, at the experimental temperature and t and t_o are the respective flow times for the same volume of solution and water. Density corrections were not made since it was found that these were negligible[68]. The solvent flow time was always longer than 200 seconds. At least four flow-time measurements were made at each concentration and a mean deviation from the mean of all measurements not exceeding 0.1 second was required. The temperature of the bath was controlled to an accuracy of $\pm$ 0.1°C. The measurements were made at 30°, 35°, 40°, 45°C.

RESULTS AND DISCUSSION

The effect of addition of KBr on the relative viscocity (η/η_o) of 0.1 m CTAB solution at 303.16 K is illustrated in Fig. 6. When a salt is added to a surfactant solution and its concentration reaches a threshold value, non spherical micelles form because the presence of salt ions near the polar heads of the surfactant molecules decrease the repulsion force between the head groups. A reduction in the repulsion makes it possible for the surfactant molecules to approach each other more closely and form larger aggregates which requires much more space for the hydrophobic chains. This leads to a sharp rise in η/η_o; in the present system (of 0.1 m CTAB) it occurs around 0.1 m KBr indicating the formation of larger aggregates[56,91] (rod-shaped micelles); this being the reason of choosing 0.1 m CTAB + 0.1 m KBr system for the detailed study of the effect of n-alkylamines and temperature.

Figures 7(a) to (d) show the variation of η/η_o with concentration of added amines at 303.16 K, 308.16 K, 313.16 K and 318.16 K. Viscosity data for different amines at different temperatures are given in Table I. Data in Table I and Figures 7(a) to (d) indicate that the addition of an amine may either decrease or increase the viscosity of starting solution (0.1 m CTAB + 0.1 m KBr). It is further seen that the increase or decrease of viscosity depends upon the chain length and the nature of added amines. With C_6, C_7 and C_8-amines, the viscosity first rises abruptly followed

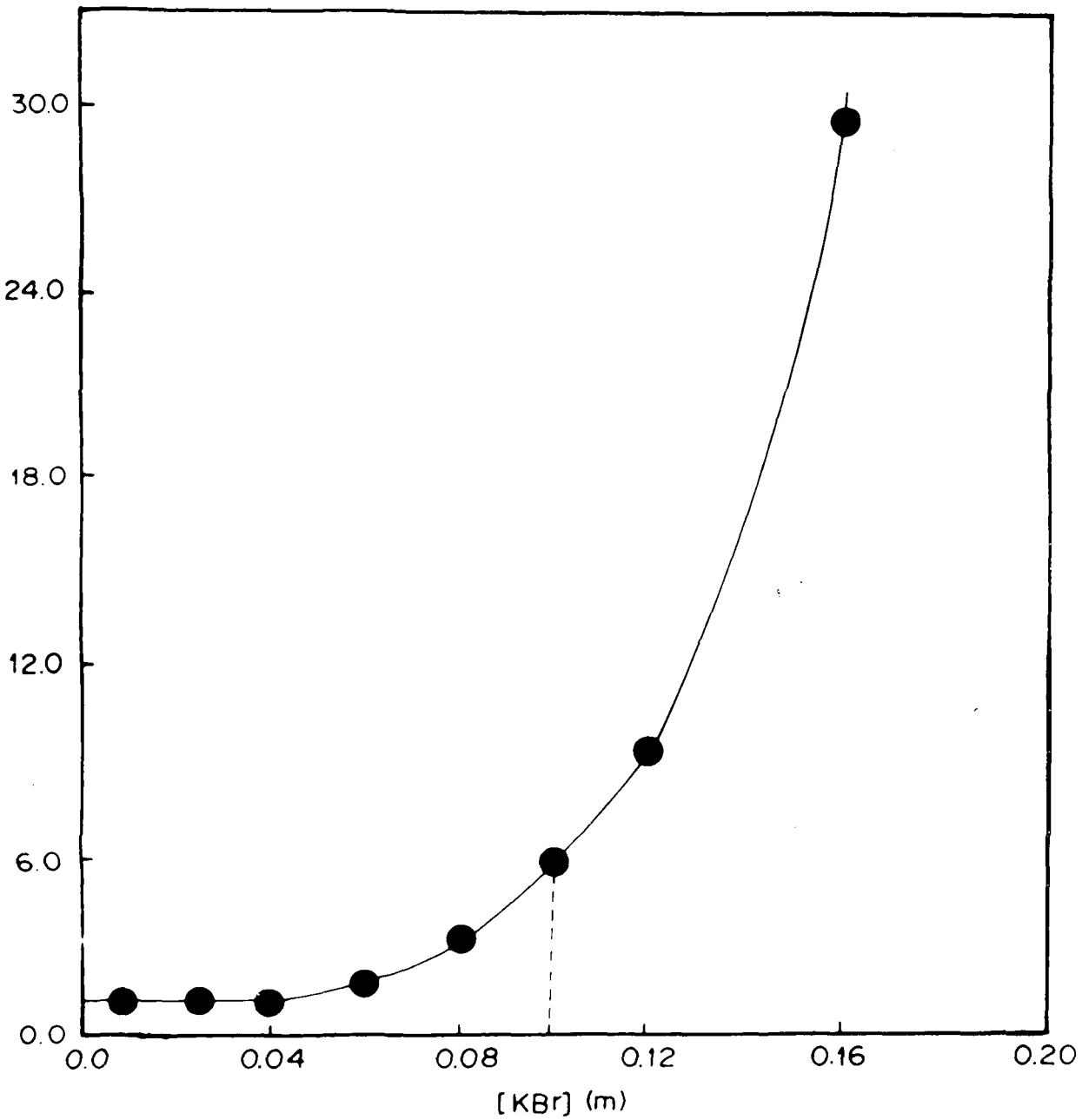


Fig. No. 6: Effect of KBr concentration on the relative viscosity of 0.1 m CTAB micellar solution at 303.16 K.

Table - I

Relative viscosities of 0.1 m CTAB + 0.1 m KBr in presence of n-amines at different temperatures.

Amine	Amine concentration (mol. kg^{-1})	Relative viscosities (η/η_o) t (°C)			
		30	35	40	45
n-Butylamine	0	4.77	2.82	1.94	1.48
	0.100	1.79	1.43	1.31	1.22
	0.150	1.56	1.38	1.28	1.20
	0.200	1.31	1.23	1.22	1.19
	0.600	1.39	1.36	1.35	1.34
	0.700	1.40	1.38	1.37	1.35
n-Hexylamine	0.020	6.69	3.76	1.81	1.64
	0.050	8.07	4.29	2.67	1.91
	0.100	5.29	3.75	2.67	2.04
	0.175	3.65	2.73	2.50	2.09
	0.250	3.18	2.79	2.54	2.34
	0.350	2.97	2.89	2.72	2.57
n-Heptylamine	0.025	31.60	12.80	5.91	3.33
	0.060	115.02	46.09	16.49	7.64
	0.075	117.20	48.85	22.13	10.69
	0.100	97.14	47.91	23.84	10.99
	0.125	45.10	17.36	11.96	7.90
n-Octylamine	0.010	11.85	5.10	2.77	1.91
	0.020	73.52	20.70	8.74	4.26
	0.030	259.99	30.86	10.33	4.18
	0.040	532.84	131.78	35.90	13.05
	0.060	678.58	251.47	89.90	37.82
	0.075	190.69	175.86	135.83	84.94

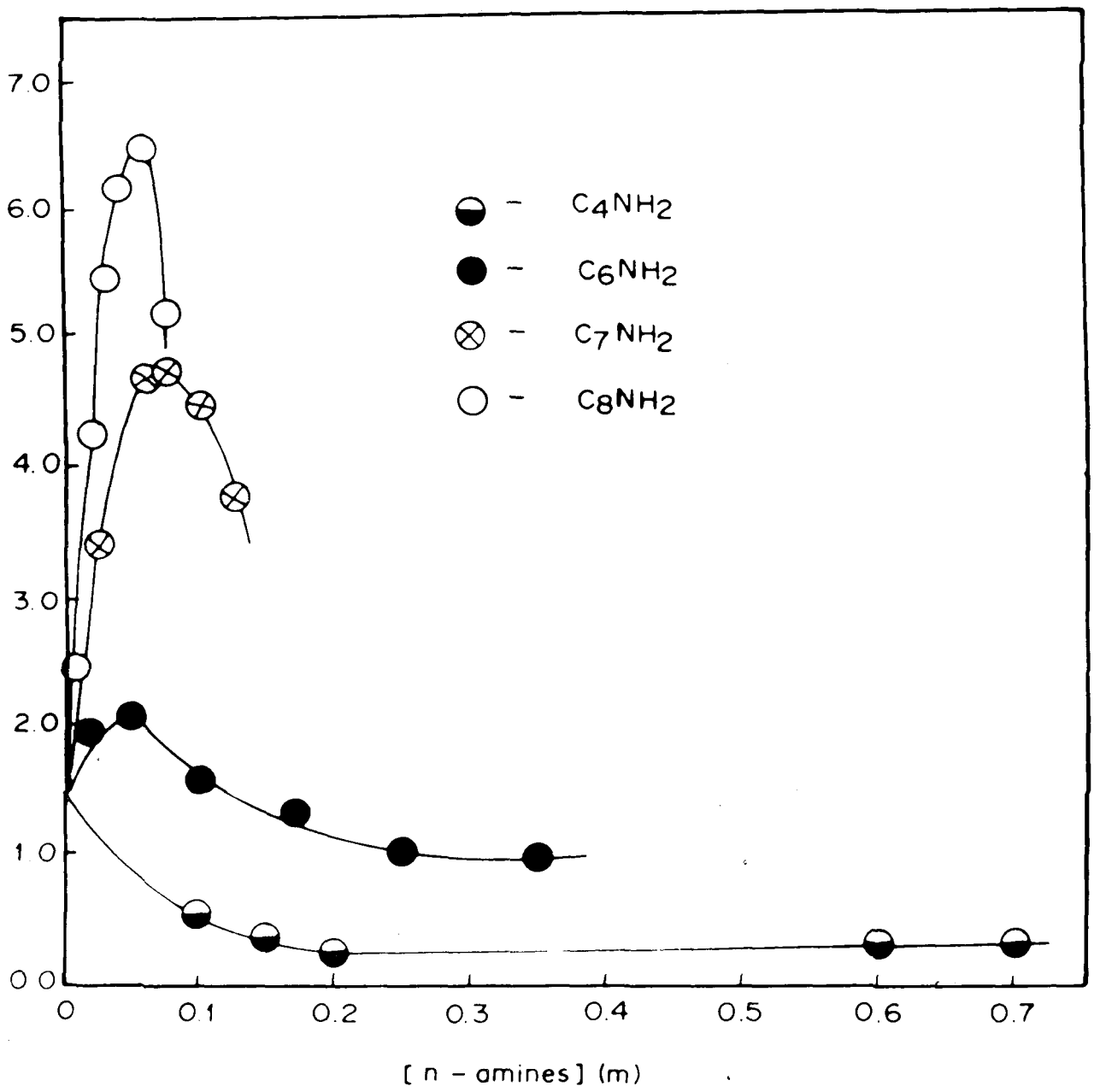


Fig. No. 7(a) Logarithms of relative viscosities of 0.1 m CTAB + 0.1 m KBr solutions as a function of added n-amines at 303.16 K.

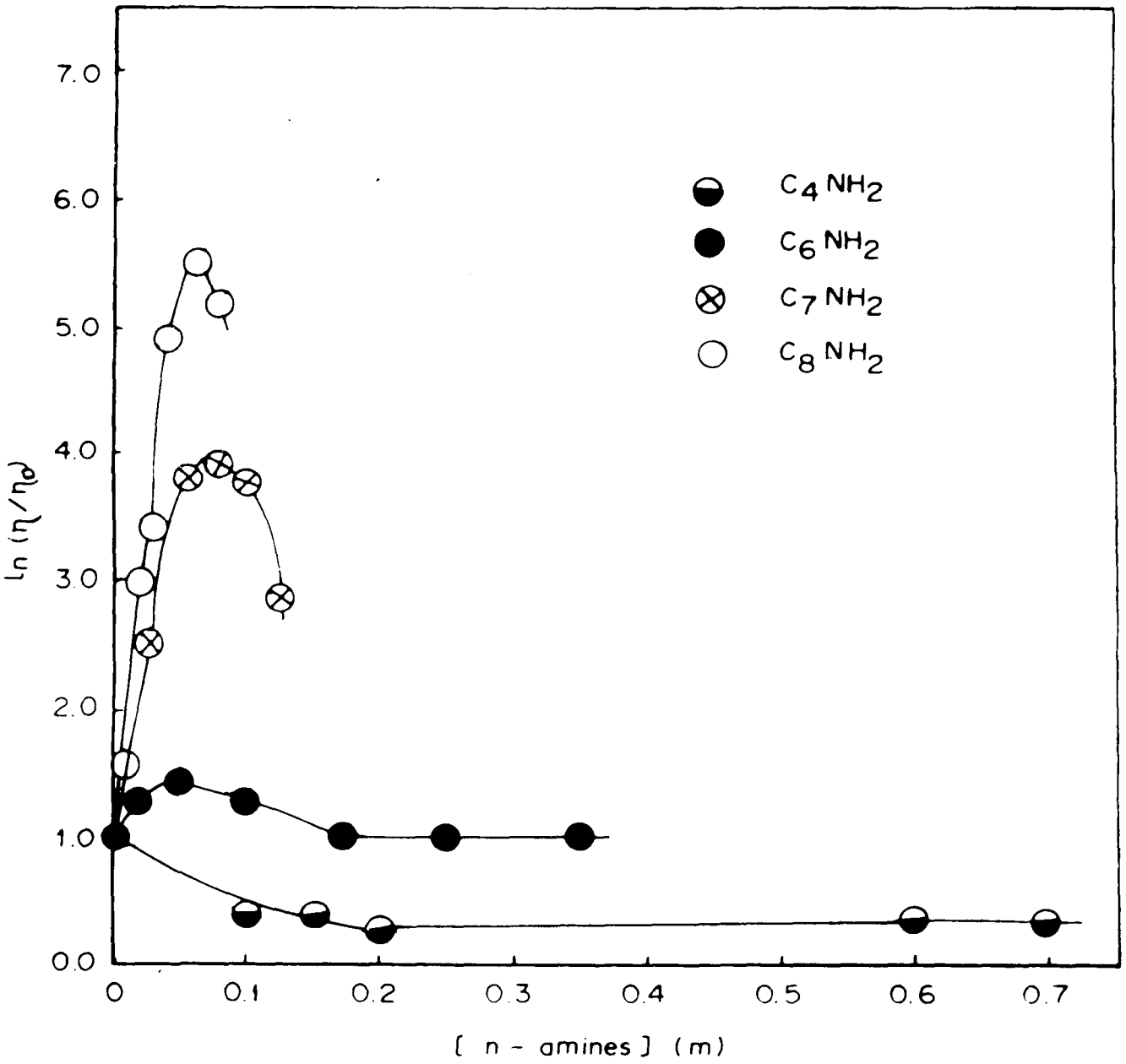


Fig. No. 7(b) : Logarithms of relative viscosities of 0.1 m CTAB + 0.1m KBr solutions as a function of added n-amines at 308.16 K.

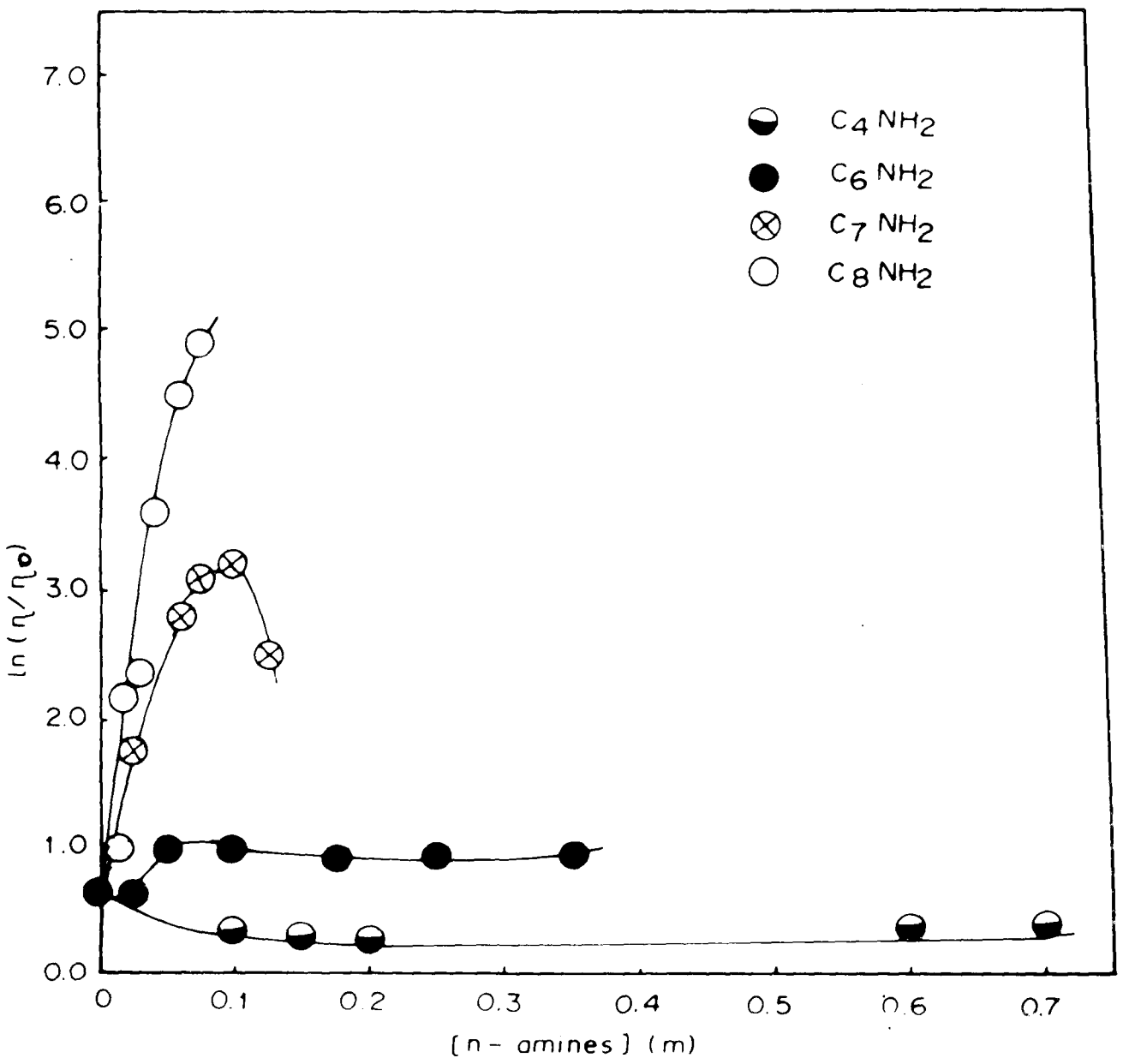


Fig.No.7 (c) : Logarithms of relative viscosities of 0.1 m CTAB + 0.1 m KBr solution as a function of added n - amines at 313.16 K

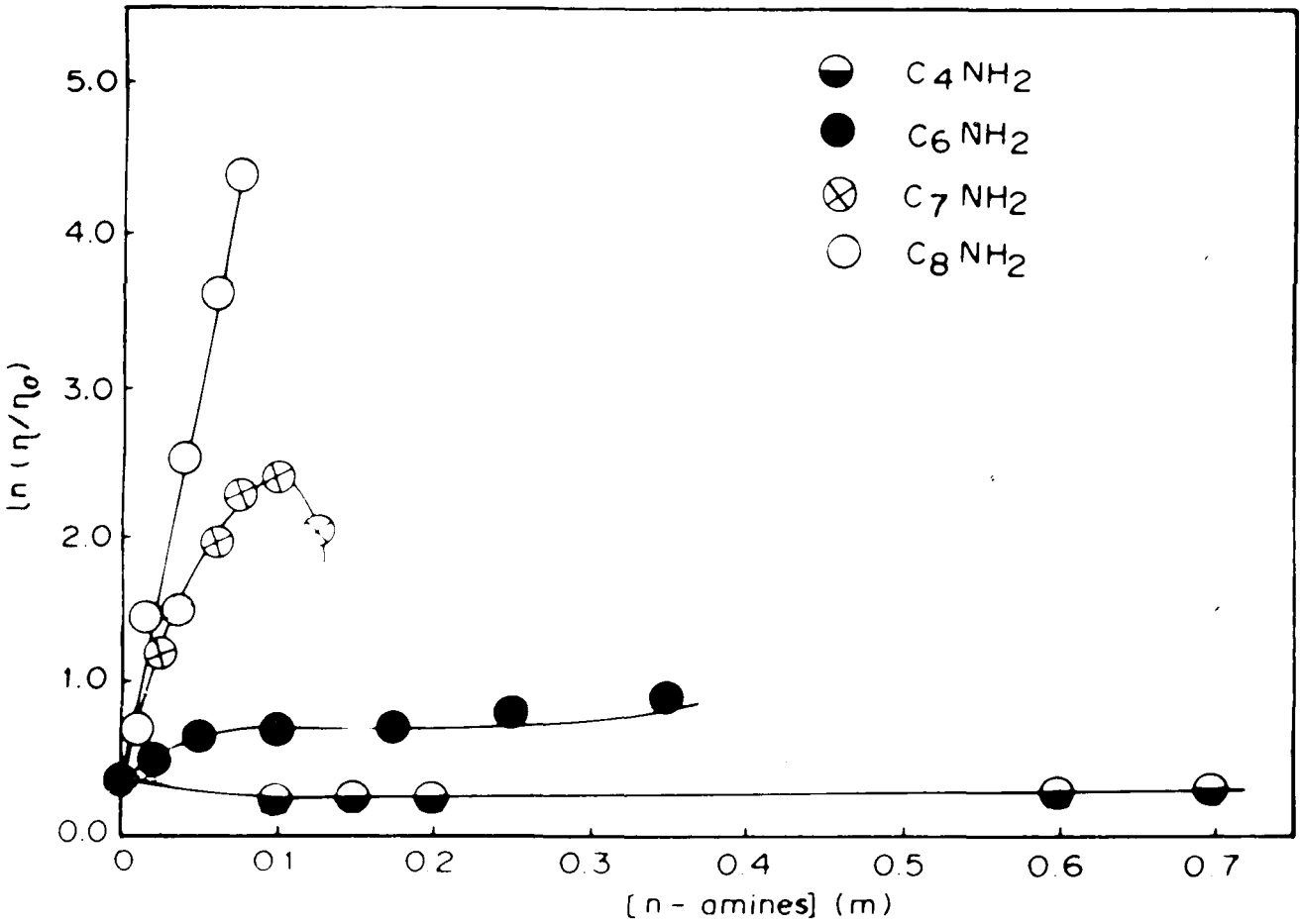


Fig .No. 7(d) : Logarithms of relative viscosities of 0.1m CTAB + 0.1m KBr solutions as a function of added n-amines at 318.16 K

by decrease in viscosity. The effect was progressively more pronounced for C_7 and C_8 amines. In case of C_4NH_2, viscosity decreases right from the beginning. The viscosity increments at low concentrations of higher amines (C_6-C_8) can be interpreted in terms of the formation of large micelles owing to their solubilization/incorporation into the micelles. The decrease in the viscosity on a further addition of these amines is a result of the breaking of larger micelles into small aggregates. Addition of C_4NH_2 results in breaking of initially present rod-shaped micelles to spherical with a concomitant decrease in the viscosity value comparable to globular micellar solution. The preceding discussion reflects that larger amines solubilize preferentially in micellar solution and lower the surface charge density which is responsible for micellar sphere-to-rod transition. Further addition of the amine beyond the optimum concentration affects the water structure predominantly, resulting in the breaking of giant aggregates to relatively smaller ones and hence a gradual decrease in viscosity is observed. The behaviour of C_4NH_2 different than others is due to the hydrophilic nature of this amine, it is partitioned more in the aqueous phase; hence this affects the water structure and causes the breaking of initially present large micelles in the solution[92]. Such transitions from rod-to-sphere by the addition of lower alcohols to dodecyltrimethyl ammonium bromide-sodium salicylate micelles have been reported from

light scattering measurements[93].

Fig. 8 shows the ln (η/η_o) vs. 1/T plots for different concentrations of heptylamine (similar type of plots were obtained for other amines). The observed linearity of the plots shown in Figure 8 is interpreted in terms of the relation[57]

$$\ln \eta/\eta_o = \ln A + \Delta G^*/RT \quad \ldots\ (2)$$

where A is a constant and ΔG^* is the activation free energy for viscous flow. As densities of the solutions were close to density of water, kinematic corrections were neglected, and values of ΔG^* were calculated from the slopes of these straight lines shown in Figure 8. As stated earlier, η/η_o were obtained only at four temperatures in the range of 30 to 45°C. The lack of more experimental data points does not preclude in obtaining good correlation coefficients (r). Estimation of activation parameters are, therefore, sufficiently adequate. The r and calculated ΔG^* values are shown in Table II.

Using the Gibbs-Helmholtz equation

$$\partial(\Delta G^*/T)/\ \partial(1/T) = \Delta H^* \quad \ldots\ (3)$$

alongwith the dependence of ΔG^* on T (Figure 9), the activation enthalpy (ΔH^*) for the viscous flow was calculated. The ΔH^* values reflect the energy used in the rod-to-sphere transition. When the temperature is increased by a

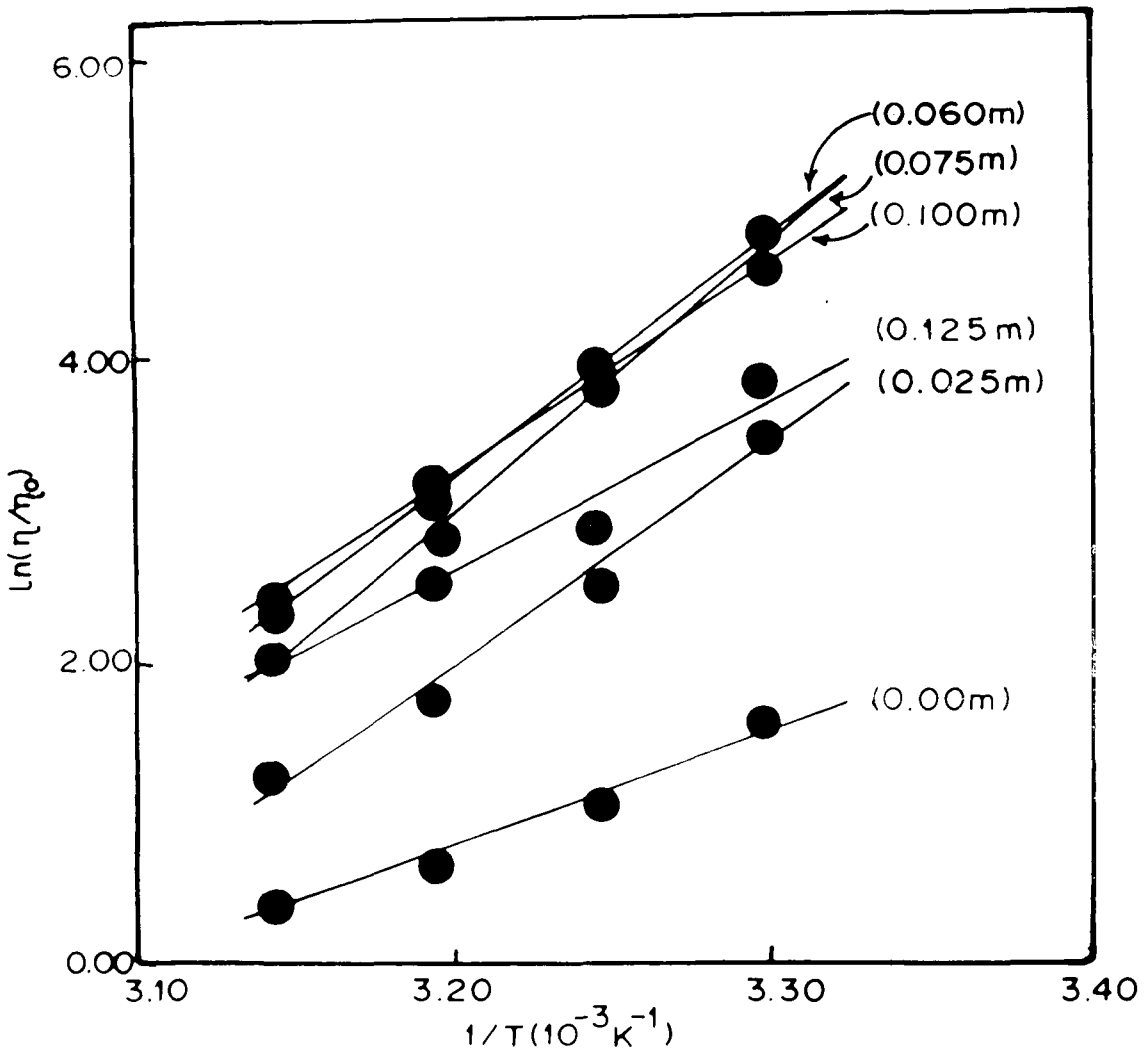


Fig. No . 8: Variation of $\ln(\eta/\eta_0)$ with $1/T$ for 0.1 m CTAB + 0.1 m KBr solutions in the presence of various concentration of n-heptyl amine maintioned in ( ).

small value dT the total energy added to the system is $C_p dt$, where C_p is the heat capacity at constant pressure. This amount of energy will partially be spent on "evaporating" some of the amphiphiles previously attached to the micelles. At high temperature these evaporated surfactant molecules are unable to remain in solution, so it is a necessary consequence that they form new micelles consisting of a smaller number of monomers. This mechanism is involved in transition of rod-shaped micelles to spherical ones at elevated temperatures.

The obtained $\triangle H^*$ values (from Figure 9) are also given in Table II. The values of $\triangle G^*$ and $\triangle H^*$ show that $\triangle H^*$ covers the total contribution to $\triangle G^*$ and, therefore, the entropic contribution is negligible. It may be noticed that the observed linearity in the ln η/η_o vs. 1/T plots (Figure 8) indicates that enthalpic contribution to $\triangle G^*$ is independent of temperature.

Figure 10 shows the variation of $\triangle H^*$ with concentration of added amines. From Table II and Figure 10, it may be seen that $\triangle G^*$ and $\triangle H^*$ values are highly dependent on the nature and concentration of added amines. The higher values of $\triangle H^*$ correspond to the formation of larger aggregates (elongated rods), and low values towards the smaller aggregates (spherical micelles). The magnitude of $\triangle G^*$ and $\triangle H^*$ for different amines indicates that higher chain length amines are capable to induce the growth process of

Table - II

Activation free energies and enthalpies for the viscous flow of 0.1 m CTAB + 0.1 m KBr solution in presence of n-amines and correlation coefficients (r) for the linear variation of $\ln \eta/\eta_o$. with 1/T.

Concetration of amine ($mol.kg^{-1}$)	$\ln (\eta/\eta_o)$				10^4 slope (K)	ΔG^* (k cal/ mol)	ΔH^* (k cal/ mol)	
T =	303.16 K	308.16 K	313.16 K	318.16 K				
$\frac{1}{T} \times 10^3$ =	3.299 K^{-1}	3245 K^{-1}	3.1934K^{-1}	3.143 K^{-1}				
0	1.5620	1.0370	0.6610	0.3920	0.74907	14.884	14.881	0.9981
n-Butylamine								
0.100	0.5822	0.3570	0.2690	0.1970	0.24025	4.774	4.775	0.9943
0.150	0.4420	0.3180	0.2460	0.2020	0.15287	3.038	3.037	0.9987
0.200	0.2680	0.2080	0.2040	0.1920	0.04496	0.893	0.894	0.9873
0.600	0.3280	0.3500	0.3040	0.2970	0.02651	0.527	0.527	0.9972
0.700	0.3380	0.3240	0.3180	0.3040	0.02076	0.413	0.412	0.9919
n-Hexylamine								
0.020	1.9010	1.3240	0.5940	0.4940	0.95548	18.985	18.989	0.9995
0.050	2.0880	1.4560	0.9820	0.6470	0.92455	18.371	18.372	0.9928
0.100	1.6650	1.3220	0.9820	0.7130	0.61505	12.221	12.223	0.9992
0.175	1.2950	1.0040	0.9150	0.7370	0.33982	6.752	6.751	0.9892
0.250	1.1560	1.0260	0.9320	0.8500	0.19493	3.873	3.875	0.9958
0.350	1.0530	1.0610	1.0000	0.9440	0.07412	1.473	1.473	0.9976

Contd..

Contd.. Table II

n-Heptylamine								
0.025	3.4500	2.4900	1.7700	1.2030	1.4374	28.561	28.563	0.9949
0.060	4.7400	3.8300	2.8020	2.0330	1.7602	34.975	34.981	0.9990
0.075	4.7600	3.8880	3.0970	2.3690	1.5323	30.447	30.444	0.9970
0.100	4.5760	3.8690	3.1700	2.3900	1.3948	27.715	27.708	0.9991
0.125	3.8080	2.8500	2.4800	2.0670	1.0794	21.448	21.449	0.9847
n-Octylamine								
0.010	2.4730	1.6300	1.0200	0.6460	1.1746	23.339	23.340	0.9980
0.020	4.2900	3.0300	2.1670	1.4500	1.8081	35.927	35.933	0.9943
0.030	5.5600	3.4290	2.3350	1.4300	2.6017	51.696	51.695	0.9814
0.040	6.2780	4.8800	3.5800	2.5700	2.3917	47.526	47.526	0.9985
0.050	6.5200	5.5270	4.4980	3.6330	1.8641	37.040	37.044	0.9997
0.075	5.2500	5.1690	4.9100	4.4400	0.51418	10.217	10.215	0.9896

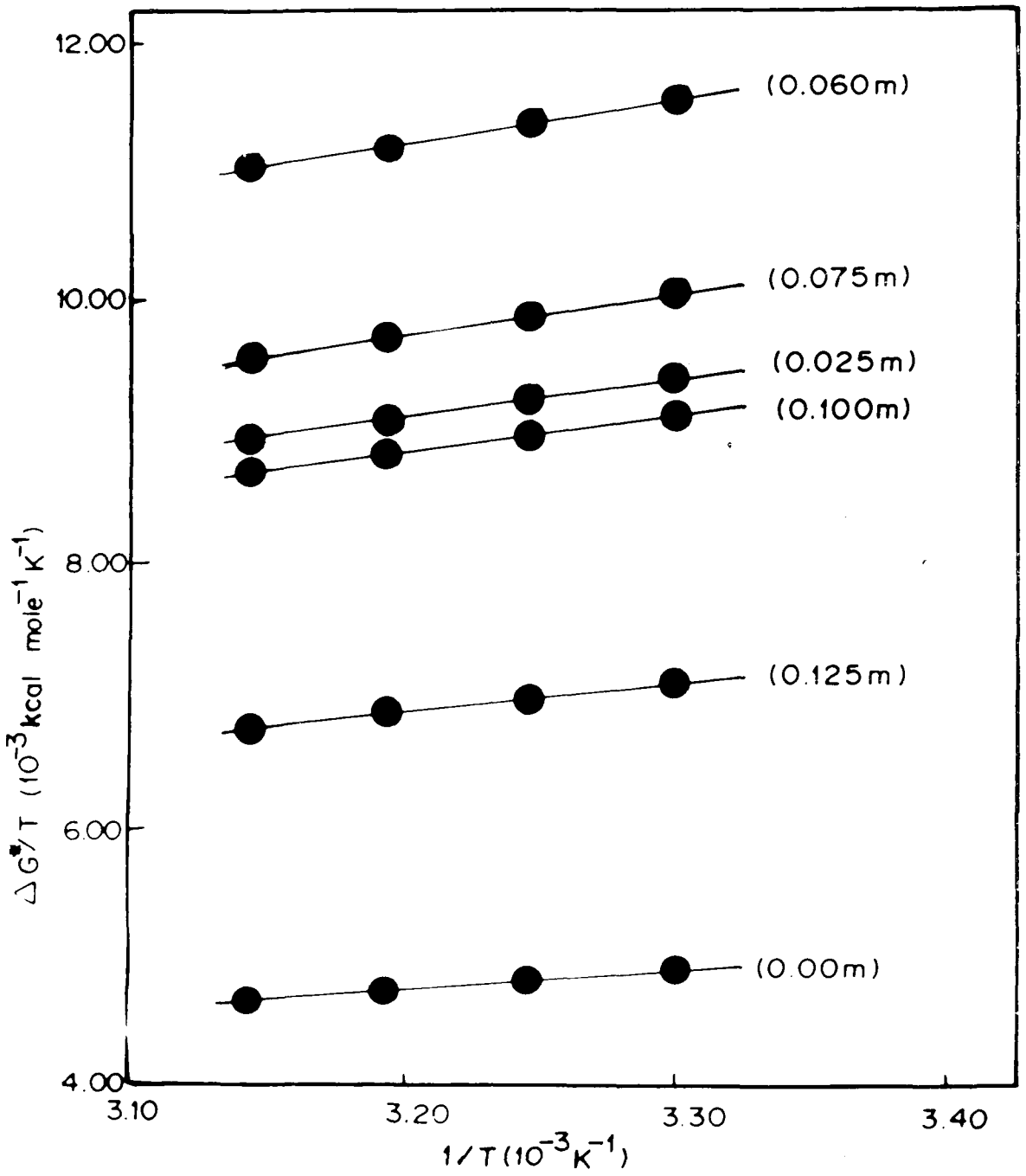


Fig. No. 9: Gibbs – Helmholtz plots for 0.1 m CTAB + 0.1 m KBr in the presence of various concentration of n-heptyl amine mentioned in ( )

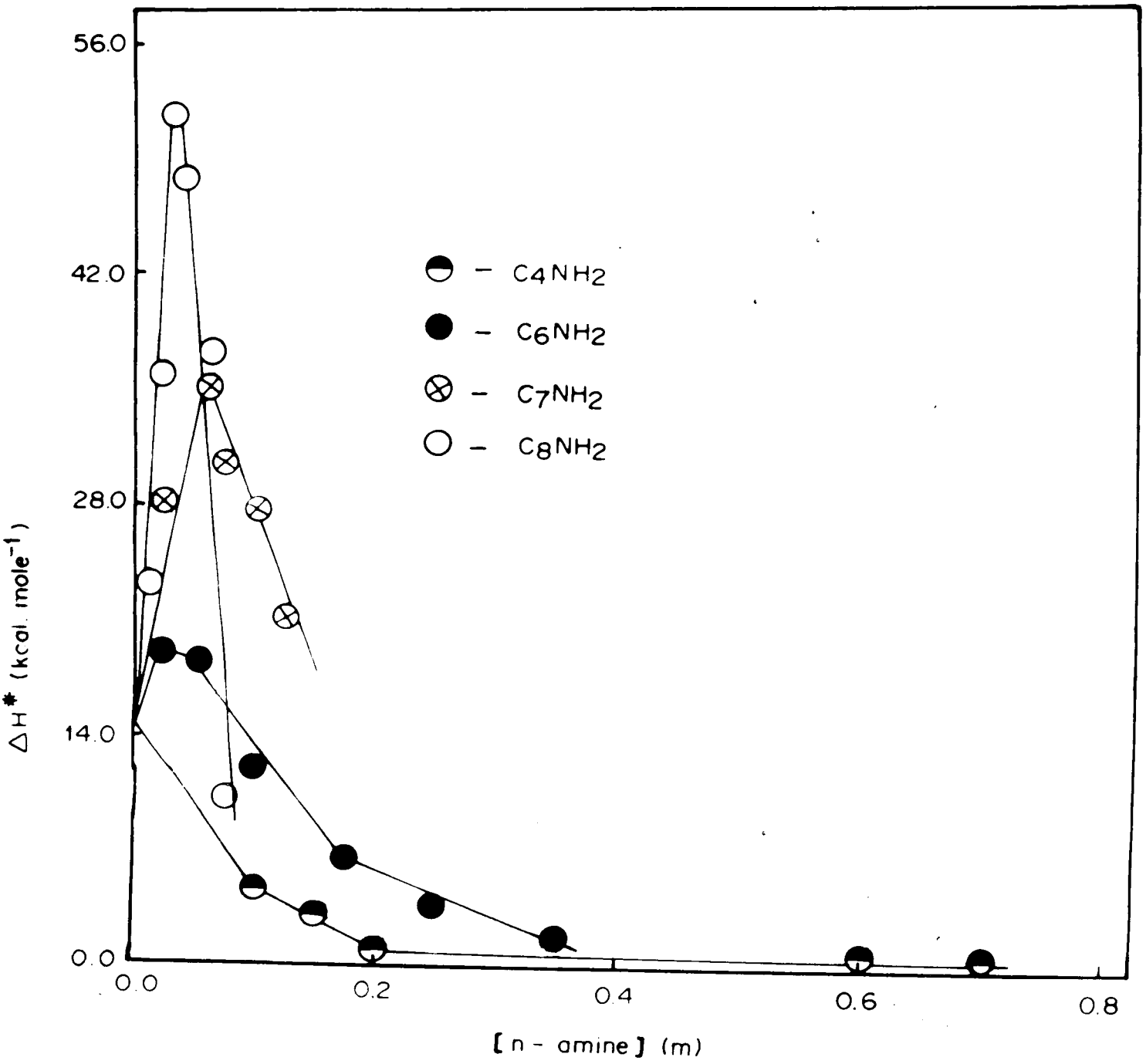


Fig. No. 10: Variation of activation enthalpy (ΔH^*) for the viscous flow of 0.1 m CTAB + 0.1 m KBr solutions as a function of added n-amines.

micelles upto a optimum concentration, beyond which a solvent structure comes in picture. While the low values for ΔH^* for C_4NH_2 show that the water structure factor plays an important role with hydrophilic additive with a concomitant breaking of larger aggregates. The behaviour of these amines is due to the combined effect of two opposite effects, namely, partitioning in micellar phase and partitioning in bulk solvent. At higher concentrations the latter effect plays an important role in breaking the larger aggregates.

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